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# The Direct Radiolysis and the Radiation-Sensitized Hydrogenation of Ethylene<sup>1</sup>

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#### INTRODUCTION

The lack of information in the literature pertaining to the radiation chemistry of ethylene is quite surprising. There have been, to the author's knowledge, only four papers dealing with this subject published since 1925.

Mund and Koch (1), in probably the first investigation into the radiolysis of ethylene, observed the formation of liquid hydrocarbons, as well as an evolution of permanent gases  $(CH_4 + H_2)$  whose rate of formation appeared to be about 10% of the rate of ethylene disappearance. Somewhat later Lind *et al.* (2) studied  $\alpha$ -particle radiolysis in more detail and found ethylene to react with an ion-pair yield of 5.1, with hydrogen and methane formation occurring with a combined ion-pair yield of about 0.8. Using the values of Jesse and Sadauskis (3) for the average energy required to produce an ion pair, these ion-pair yields correspond to G values of -18.2 and 2.9, respectively. No other products were reported by these authors.

Lewis *et al.* (4) reported the  $\gamma$ -ray-induced polymerization of ethylene at room temperature and pressures ranging from 17 to 109 atmospheres. They observed the formation of white solid polyethylene with G values for ethylene consumption being very dependent on total dose and ranging from 0 to as high as 2000.

Recently an electron radiolysis of ethylene has been reported (5) in which gaseous reaction products consisting of butane, acetylene, hydrogen, methane, ethane, and butene were observed; the liquid products consisted of C-6 and C-8 aliphatic hydrocarbons, aromatics, and olefins. Quantitative energy yield values, if measured in this work, were not available to the author.

The literature situation regarding the radiation-induced hydrogenation of ethylene is similar to that of the direct radiolysis. Lind *et al.* (2) report a few in-

<sup>1</sup> Based on a paper presented before the annual meeting of the Radiation Research Society, Pittsburgh, May 18-20, 1959, as part of the Symposium on Radiation Chemistry of Gases in honor of Dr. S. C. Lind on the occasion of his eightieth birthday. The Symposium was organized by Dr. Leon M. Dorfman, and he and Dr. A. O. Allen served as chairmen of the sessions.

conclusive experiments under conditions which most probably would not give results much different from those obtained in the direct radiolysis. Mikhailov *et al.* (5) mention that dilution of the ethylene with hydrogen did affect both the conversion of ethylene and the yield of gaseous products.

With such a scarcity of information on an important compound, ethylene radiation chemistry seemed to us to be a field in need of much investigation.

## EXPERIMENTAL PROCEDURE

The radiation employed in this work was the electron beam from a 2-Mev Van de Graaff electrostatic accelerator. In all experiments the accelerating voltage was maintained at 2.0 Mv and the electron beam current at approximately 5  $\mu$ a.

The irradiation vessels and procedures have been described previously (6). The radiation-induced polymerization of acetylene was used as a dosimeter; the details of the method were described in a previous publication (7).

Phillips research-grade ethylene, having a stated purity of 99.9+ mole %, was frozen out in liquid nitrogen and then allowed to distill slowly into an evacuated  $(10^{-6} \text{ mm})$  storage bulb on the vacuum system. The middle third of the frozen-out sample was collected. Hydrogen was obtained from the Matheson Company, and argon from the Air Reduction Sales Company. Both were used without further purification.

Quantitative analysis of C-1 through C-6 hydrocarbons was accomplished by gas liquid partition chromatography. The use of two columns, consisting of hexadecane and benzyl cellosolve substrates on 40- to 60-mesh crushed firebrick support, enabled complete separation and determination of all hydrocarbon con-

Compound	G (75 mm)	G (150 mm)
$C_2H_4$	$-14.2 \pm 2.3$	$-15.5 \pm 1.8$
$H_2$	$1.14 \pm 0.28$	$1.28 \pm 0.19$
$CH_4$	$0.13 \pm 0.02$	$0.12 \pm 0.02$
$C_2H_2$	$1.52 \pm 0.04$	$1.46 \pm 0.10$
$C_2H_6$	$0.40 \pm 0.01$	$0.27 \pm 0.10$
$C_{3}H_{6}$	$0.26 \pm 0.02$	$0.23 \pm 0.04$
$C_{3}H_{8}$	$0.33 \pm 0.02$	$0.11 \pm 0.03$
n-C <sub>4</sub> H <sub>10</sub>	$0.50 \pm 0.03$	$0.48 \pm 0.05$
cis-C4H8-2	$0.21 \pm 0.12$	$0.12 \pm 0.04$
trans-C <sub>4</sub> H <sub>8</sub> -2	$0.12 \pm 0.02$	$0.14 \pm 0.05$
1-C <sub>4</sub> H <sub>8</sub> (or iso)	$0.17 \pm 0.04$	$0.14 \pm 0.04$
n-C <sub>5</sub> H <sub>12</sub>	$0.13 \pm 0.05$	$0.06 \pm 0.02$
n-C.H.	$0.16 \pm 0.06$	$0.13 \pm 0.04$

TABLE I

100-Ev Yields in Ethylene Radiolysis at 25°C	100-Ev	V YIELDS IN	ETHYLENE	RADIOLYSIS	$\mathbf{AT}$	25°(	2
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This content downloaded from 134.117.10.200 on Mon, 15 Feb 2016 23:32:00 UTC All use subject to JSTOR Terms and Conditions stituents in the aforementioned range. Hydrogen was determined mass spectrometrically.

## RESULTS AND DISCUSSION

Ethylene radiolysis. The gaseous products of the direct electron radiolysis of ethylene and their 100-ev yields for initial ethylene pressures of 75 and 150 mm are shown in Table I. All such G values were obtained by the measurement of initial slopes of plots in which the amount of substance formed (or consumed, as in the case of ethylene) was plotted versus the energy absorbed. A typical such plot showing acetylene and ethane formation at 150 mm is shown in Fig. 1.

The course of the reaction, as reflected by the G values, appears to be independent of initial ethylene pressure. Although there is a variation in the G values for ethane and propane with pressure that is outside the estimated experimental error, it is more likely, in the author's opinion, that the observed variation is from an experimental source rather than being characteristic of the reaction. In addition, the complexity of the reaction, as indicated by the presence of twelve gaseous products, is made even more evident when it is realized that only about one-third



FIG. 1. Acetylene and ethane formation at 150 mm in the direct radiolysis of ethylene.

of the ethylene that has reacted is accounted for by the gaseous products. Thus polymerization of ethylene to a material of low vapor pressure must be the predominating process.

The near equality of the hydrogen and acetylene G values immediately suggests that their formation is similar to that involved in the mercury-photosensitized decomposition of ethylene (8); in this case, acetylene and hydrogen are formed as the result of the decomposition of an excited ethylene molecule. However, a serious objection to this suggested mode of formation is the apparent independence of  $G(C_2H_2)$  with respect to pressure. Collisional deactivation of excited ethylene, which results in a decrease in the quantum yield of the mercury-photosensitized decomposition (8) and which would be expected to result in a decrease in  $G(C_2H_2)$ , will, of course, be more probable at higher pressures. Although the data in Table I refer to only a twofold variation in pressure, the results of experiments in which the pressure is increased severalfold by the addition of argon (and which are presented in a later section) confirm the conclusion that acetylene most probably is not formed from a unimolecular decomposition of excited ethylene.

One of the many ion-molecule reactions observed in ethylene (9, 10), namely,

$$C_2H_3^+ + C_2H_4 \rightarrow C_2H_5^+ + C_2H_2$$
 (1)

produces acetylene, and it is tempting to consider reaction 1 as the source of the acetylene. However, one is still faced with the difficulty of explaining the nearly equal hydrogen formation rate, the origin of the many other gaseous products, the polymerization, and the ultimate results of the many other known ion-molecule reactions, some of which are more probable than reaction 1. Thus, although we feel that the key to the understanding of the radiation chemistry of ethylene lies in the ion-molecule reactions, we have so far been unsuccessful in relating all the ion-molecule reactions and their consequences to the observed results of the ethylene radiolysis.

Radiolysis of ethylene-argon mixtures. To investigate further the effect of total pressure on the radiolysis of ethylene, we carried out experiments in which varying amounts of argon were added to 75 mm of ethylene. The observed G values, de-

<i>a</i>	"G" for argon partial pressure of:			
Component	0 mm	75 mm	150 mm	225 mm
C <sub>2</sub> H <sub>4</sub>	-14.2	-25 (-30)	-40 (-46)	-42 (-61)
$C_2H_2$	1.52	3.0(3.2)	3.6(4.9)	4.3 (6.6)
$C_2H_6$	0.396	0.58(0.84)	0.78(1.3)	0.77(1.7)
$n-C_4H_{10}$	0.505	0.89(1.1)	1.0 (1.6)	$1.1 \ (2.2)$

TABLE II EFFECT OF ARGON ON THE RADIOLYSIS OF ETHYLENE

This content downloaded from 134.117.10.200 on Mon, 15 Feb 2016 23:32:00 UTC All use subject to JSTOR Terms and Conditions fined in this instance by the number of molecules formed or consumed per 100 ev of energy *absorbed by ethylene*, and determined in the same manner as those shown in Table I, are shown in Table II. The values shown parenthetically were calculated by dividing the values obtained in the absence of argon by the fraction of the energy absorbed by ethylene. Thus, these would be the observed values if all the energy absorbed by the argon was as effective in producing reaction as is energy absorbed by the ethylene. Figure 2 shows typical results for the product formation in a mixture of 75 mm of ethylene and 75 mm of argon.

The increase in the G values with argon concentration is evidence of interaction between argon and ethylene—that is, energy is somehow transferred from the argon to the ethylene, be it a transfer of charge or of excitation. Such transfer manifests itself as an increase in the rate of ethylene conversion, an effect that has been noted previously in acetylene (11, 12), butadiene (12), and several inorganic



FIG. 2. Product formation in radiolysis of ethylene (75 mm)-argon (75 mm) mixture.

## TABLE III

Comment	Rela	tive $G$ at argon	partial pressu	re of:
Component	0 mm	75 mm	150 mm	225 mm
$C_2H_4$	9.4	8.3	11	9.8
$C_2H_2$	1.0	1.0	1.0	1.0
$C_2H_6$	0.26	0.19	0.22	0.18
$n-C_4H_{10}$	0.33	0.30	0.28	0.26

EFFECT OF ARGON ON THE COURSE OF THE RADIOLYSIS

gas radiolyses (11). The G values shown in Table III are those of Table II but calculated relative to  $G(C_2H_2) = 1$ . The fact that  $G(C_2H_2)/G(-C_2H_4)$  is independent of pressure over a wider range than is shown in Table I is confirmatory evidence that acetylene is not formed in a unimolecular dissociation of excited ethylene. If acetylene were formed in this way, all reaction paths of ethylene conversion would have to be unimolecular also, and that is very unlikely. Although there may be a trend in the  $G(C_4H_{10})/G(C_2H_2)$  ratio with argon pressure, the observed variation is within experimental error and, in our opinion, should be considered as constant. The constancy, or rather the very small variation in relative Gvalues with varying argon pressure, indicates that the distribution of entities derived from ethylene and responsible for the observed reaction is the same whether the ethylene receives the initial energy from 1.7-My electrons or from argon ions and/or excited argon atoms. It thus appears that the immediate precursors to the major products are identical whether argon or ethylene absorbs the electron beam energy. Moreover, the very high specific reaction rates of the ion-molecule reactions initiated by electron impact on ethylene (9, 10) force one to conclude that such reactions are occurring in irradiated ethylene. Therefore, although the evidence is certainly not compelling, it is at least suggestive that the following processes represent the argon-ethylene interaction:

$$A^{+} + C_{2}H_{4} \rightarrow C_{2}H_{4}^{+} + A$$
$$A^{*} + C_{2}H_{4} \rightarrow C_{2}H_{4}^{+} + A$$

where  $A^*$  represents an argon atom in an excited state that is at least 10.5 volts above the ground state.

Comparison of the G values of Table II with the values in parentheses indicates that the energy transfer from argon to ethylene is surprisingly efficient, especially at low argon partial pressures. As the argon partial pressure is increased, however, the efficiency seems to decrease, as would be expected because of the increased probability of argon ion-electron recombination and of collision of argon-excited atoms with argon with degradation of the energy. Sensitized hydrogenation of ethylene. Photosensitized hydrogenation reactions are based on the initial formation of hydrogen atoms by the interaction of an excited metal atom with molecular hydrogen (8). The hydrogen atoms so formed attack a substrate to initiate the observed chemical conversion. For example, in the mercury-photosensitized hydrogenation of ethylene (8), the following mechanism explains the experimental facts at room temperature:

$$\mathrm{Hg}(^{3}P_{1}) + \mathrm{H}_{2} \to 2\mathrm{H} + \mathrm{Hg}(^{1}S_{0}) \tag{1}$$

$$\mathbf{H} + \mathbf{C}_{2}\mathbf{H}_{4} \to \mathbf{C}_{2}\mathbf{H}_{5} \tag{2}$$

$$C_2H_5 + C_2H_5 \to C_2H_6 + C_2H_4$$
 (3)

$$C_2H_5 + C_2H_5 \rightarrow C_4H_{10} \tag{4}$$

The quenching cross section of ethylene for  $Hg(^{3}P_{1})$  atoms is about eight times as large as that of hydrogen (8); consequently, even at high ratios of hydrogen to ethylene a considerable amount of energy is absorbed by the ethylene. However, under hydrogenation conditions the total pressure of the system is high, and the consequences of energy absorption by the ethylene (unimolecular dissociation of excited ethylene to acetylene and hydrogen) is kept to a minimum by deactivating collisions. In other words, under hydrogenation conditions reaction 6 is favored over reaction 5, and reactions 1 to 4 completely account for the observations:

$$C_2H_4^* \to C_2H_2 + H_2 \tag{5}$$

$$C_2H_4^* + M \to C_2H_4' + M \tag{6}$$

In reaction 6 the prime denotes a lower state of excitation than the asterisk.

Now consider the case of subjecting a mixture of hydrogen and ethylene to ionizing radiation. The absorption of energy by hydrogen will produce ionization, i.e.,

$$\mathbf{H}_2 \xrightarrow{} \mathbf{W} \xrightarrow{} \mathbf{H}_2^+ + e \tag{7}$$

and reaction 7 will be followed very quickly by reaction 8 (13, 14):

$$H_{2}^{+} + H_{2} \rightarrow H_{3}^{+} + H$$
 (8)

Neglecting the admitted possibility of proton transfer from  $H_3^+$  to ethylene, we can expect  $H_3^+$  to undergo only neutralization, i.e.,

$$\mathrm{H}_{3}^{+} + e \to \mathrm{H}_{2} + \mathrm{H} \text{ (or 3H)}$$

$$\tag{9}$$

The result, of course, of reactions 7 to 9 is that an ionization event in hydrogen has resulted in the formation of two or four hydrogen atoms. These hydrogen atoms will initiate the chemical conversion of ethylene through reactions 2 to 4.

However, there is a complicating factor here that is not present in the photosensitized situation. As in the photosensitized case, the ethylene (containing 16 electrons as compared to 2 for hydrogen) will absorb appreciable amounts of energy even at high ratios of hydrogen to ethylene. Here the similarity ends, for the con-

sequences of energy absorption by ethylene are independent of pressure, as shown in the first two sections of this paper, and reactions 7 to 9 followed by reactions 2 to 4 will not account completely for the results. The rather unselective consequences of energy absorption by ethylene will be superimposed on the mechanism of reactions 7 to 9 followed by reactions 2 to 4.

The solution to the problem of improving the specificity of hydrogen atom initiation by ionizing radiation lies in the fact that rare gas ions will abstract hydrogen atoms from hydrogen (13). For example, if we were to irradiate argon-hydrogen mixtures, the following would occur, in addition to reactions 7 to 9:

$$\mathbf{A} \longrightarrow \mathbf{A}^+ + \mathbf{e} \tag{10}$$

$$A^+ + H_2 \rightarrow AH^+ + H \tag{11}$$

$$\mathbf{A}\mathbf{H}^{+} + e \to \mathbf{A} + \mathbf{H} \tag{12}$$

Thus energy absorption by argon has identical results to that by hydrogen. In addition, since argon will absorb energy at a much greater rate than hydrogen and somewhat faster than ethylene, the addition of argon to a hydrogen-ethylene system should result in increased specificity with respect to hydrogen atom attack.

The irradiation of mixtures of 30 mm of ethylene, 300 mm of hydrogen, and partial pressures of argon ranging from zero to 400 mm provided the following experimental facts:

1. The only significant products are *n*-butane, ethane, acetylene, and propane, which account for about 70 to 80% of the ethylene reacted. This is in contrast with the results for pure ethylene.

2. The initial rate of acetylene formation is independent of argon concentration.

3. The initial rates of formation of butane and ethane increase with argon concentration.

4. The ratio of ethane to butane increases markedly at very high conversions.

5. Propane is a minor constituent except in experiments at the highest argon pressures that were carried to high ethylene conversion. Restricting ourselves to rates extrapolated to zero time, we may neglect propane for the moment.

These facts are consistent with the occurrence of reactions 2 to 4 and 7 to 12 and with the acetylene formation occurring only as the result of energy absorption by ethylene. Assuming these reactions we can easily see that under conditions of constant hydrogen and ethylene concentrations

$$\left[\frac{R(C_4H_{10})}{R(C_2H_2)}\right]_0 = \alpha + \beta(A)$$
(13)

and

$$\left[\frac{R(C_2H_6)}{R(C_2H_2)}\right]_0 = \alpha' + \beta'(A)$$
(14)

with

$$\frac{\beta'}{\beta} = \frac{k_3}{k_4} \tag{15}$$

Since ethylene is depleted very rapidly, the acetylene formation rate decreases very rapidly with conversion. Hence, it is essential to extrapolate rate ratios to zero time. In Fig. 3 is shown the butane-to-acetylene ratios as a function of "the time of irradiation" at various partial pressures of argon (denoted in millimeters by the number on each line of Fig. 3). The intercepts of Fig. 3 are the ratios of the initial formation rates defined in equation 13. A similar plot was constructed for the determination of the initial values of  $R(C_2H_6)/R(C_2H_2)$ .

In accordance with equations 13 and 14, Fig. 4 shows the initial rate ratios plotted against argon pressure. The functions are linear, as the mechanism requires. The ratio of the slopes,  $k_3/k_4$ , is found to be 0.39, which is in fair agreement with the value of the ratio of disproportionation to combination of ethyl radicals obtained from mercury diethyl photolysis but considerably higher than that found from azoethane and diethyl ketone photolyses (8).

If ethane is formed not only by reaction 3 but by some additional process, a high value would be expected. The fact that propane is formed and becomes significant at high conversions suggests the presence of methyl radicals. We propose that in this system the following reaction is producing methyl radicals:



$$H + C_2 H_5 \rightarrow 2 C H_3 \tag{16}$$

FIG. 3. Butane-acetylene formation rate ratio as a function of time.

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FIG. 4. Effect of argon pressure on initial formation rate ratios.

and that propane is formed by

$$CH_3 + C_2H_5 \to C_3H_8 \tag{17}$$

The additional ethane is formed either by combination of methyl radicals or, equivalently, by the stabilization of the excited ethane molecule formed in equation 16. The presence of propane appears to rule out the explanation advanced for the high value of  $k_3/k_4$  found in mercury diethyl photolysis, namely, energy carryover from the primary step.

The experimental facts thus seem to be in agreement with the mechanism given by equations 2 to 4, 7 to 12, and 16 and 17 being superimposed on the normal radiolysis of ethylene. The degree to which the sensitized hydrogenation predominates depends on the concentration of the noble gas. In this particular case, reaction 16 probably could be suppressed by reducing sufficiently the intensity of radiation. Regardless of whether this reaction does or does not occur, however, the noble gas radiation-sensitized reactions appear to provide a useful method for the generation of hydrogen atoms.

# SUMMARY

In the electron radiolysis of pure ethylene, some dozen gaseous products, increasing in mass up to n-hexane, are formed. The major products are acetylene, hydrogen, n-butane, and ethane. The G values for formation of the gaseous products and for disappearance of the ethylene are independent of pressure. Polymerization of ethylene to nonvolatile material appears to be the predominant reaction, however, since the gaseous products account for only about one-third of the ethylene reacted.

When argon is added to ethylene, an energy transfer occurs which accelerates

the reaction but does not cause any large change in the course of the reaction. This is interpreted as suggestive of ethylene ion formation as a result of energy transfer.

The irradiation of argon-hydrogen-ethylene mixtures shows that specific radiation-sensitized hydrogen atom initiation is feasible. This is due to the rapid reaction of argon ions with hydrogen molecules that was first observed in mass spectrometers.

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